

The Effect of Sintering Time on The Formation of The BPSCCO-2212 Superconductor Phase at The Levels of Ca=1.10 Using The Wet Mixing Method

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Article Information	Abstract		
Article history: Received October 22th, 2021 Received in revised form December 13th, 2021 Accepted November 29th, 2022	This research was conducted to determine the effect of sintering time on to phase formation of superconducting BPSCCO-2212 with Ca content 1.10 by calculating the level of purity of the phases formed and looking at the microstructure. The variation of sintering time was 10, 20, 30, and 40 hours using the wet mixing method. The sample was calcinated at 800 °C for 10 hours and sintered at 830 °C. The XRD's characterization result showed that the highest volume fraction obtained in BPSCCO-2212/40 hours was 86.72%, while the lowest volume fraction of BPSCCO-2212/30 hours was 13.59%, while the lowest orientation degree of BPSCCO-2212/20 hours was 7.67%. The SEM's characterization result		
Keywords: Degree of orientation, sintering time, superconductors BPSCCO- 2212, and volume fraction	shows that all samples have not been oriented, and many voids (space between the plates) are still generated.		
Article Information	Abstract		
Proses artikel: Diterima 22 Oktober 2021 Diterima dan direvisi dari 13 Desember 2021 Accepted 29 November 2022	Penelitian ini dilakukan untuk mengetahui pengaruh waktu sintering terhadap pembentukan fase superkonduktor BPSCCO-2212 pada kadar Ca 1,10 dengan menghitung tingkat kemurnian fase yang terbentuk dan melihat struktur mikronya. Variasi waktu sintering yang digunakan adalah 10, 20, 30 dan 40 jam menggunakan metode pencampuran basah. Sampel dikalsinasi pada suhu 800 °C selama 10 jam dan disintering pada suhu 830 °C. Hasil karakterisasi XRD menunjukkan fraksi volume tertingginya diperoleh pada sampel BPSCCO/40jam sebesar 86,72% Sedangkan, fraksi volume terendah adalah		
Kata kunci: Derajat orientasi, fraksi volume, superkonduktor BPSCCO- 2212, dan waktu sintering	BPSCCO-2212/30jam sebesar 53,07%. Derajat orientasi yang relatif tinggi pada sampel BPSCCO-2212/30jam sebesar 13,59%. Sementara, derajat orientasi terendah pada sampel BPSCCO-2212/20jam sebesar 7,67%. Hasil karakterisasi SEM menunjukkan bahwa semua sampel belum terorientasi dan masih banyak <i>void</i> (ruang kosong antar lempengan) yang dihasilkan.		

1. Introduction

Superconductors are materials that can conduct electric current without any resistance or resistance ($\rho = 0$) so that they can conduct electric current without the slightest loss of power. Since the discovery of superconducting materials by Dutch physicists from Leiden University HK Onnes in 1911, research on superconducting materials has continued to develop. Superconductors are increasingly being used along with technological advances, such as the super-fast trains in Japan known as MagLev (Magnetic Levitation) trains (Shimbashi and Minato-ku, 2003).

Research on superconductors is intensively carried out to comprehensively understand physical problems related to theoretical, experimental, and application aspects. One of the widely studied SKST materials is the Bi-Sr-Ca-Cu-O (BSCCO) system because its critical temperature is relatively high and does not contain toxic elements

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(Yulianti, 2002). they are also known as Bi-based superconductors. There are 3 phases in this system. The different superconductive ones are phase 2201 with Tc = 10 K, phase 2212 with Tc = 80 K, and phase 2223 with Tc = 110 K.

Synthesis of superconducting crystal Bi-2212 can be achieved through several methods, including the solid phase reaction method, the Floating Zone (FZ) method, the Self Flux method with Pb doping (Zhao et al., 2000), the Self Flux method with CaCO $_3$ and CuO (Yulianti, 2002), and the Traveling Solvent Floating Zone (TSFZ) method (Benseman, et al. 2007). Generally, these methods produce powders with a crystal size of >100 nm and require a relatively long heating time.

Dopants play an essential role in the formation of high Tc superconductors. Increasing the value of critical temperature and critical current density can be done by giving a dopant (DB Currie and AM Forest, 1988). The dopant can replace the original atoms in the superconductor with dopant atoms that are not much different in size from the original atoms. In addition, the dopant can be added. That is, adding dopant atoms to the original atoms of the superconductor. The use of Pb dopants in the synthesis of polycrystalline Bi systems, apart from facilitating the formation of the compound in question, also affects the properties of the resulting compound. Due to the similarity of ion sizes and valence requirements of Pb atoms, it is believed that the addition of Pb as a dopant result in the substitution of Bi atoms by Pb atoms in the Bi-O double layer (Nurmalita, 2011).

Research on Pb doping variations in the BPSCCO 2212 system was conducted by Pratiwi (2016) with variations in Pb doping levels used 0; 0.1; 0.2; 0.3, and 0.4, at Ca content = 1.10, calcination temperature 800°C and sintering temperature 830°C, using the solid reaction method. This study found that samples with a doping level of 0.4 had the highest volume fraction (Fv = 80.99%) and degree of orientation (P = 23.16%).

Then research on the effect of sintering temperature on CaCO3 levels $_{1.10}$ was carried out by Sari (2013) by varying the sintering temperatures to 815° C, 820° C, 825° C, 830° C using the solid reaction method. The results showed that the highest volume fraction was obtained at 830° C sintering temperature, namely Fv = 90.10%, while the highest degree of orientation was obtained at 825° C, namely P = 59.31%.

This study aims to determine the effect of sintering time on the purity level of the BPSCCO-2212 superconducting phase at Ca content of 1.10 using the wet mixing method with variations of sintering time 10 hours, 20 hours, 30 hours, and 40 hours. The aspect studied in this research is the purity level of the formed phase by calculating the volume fraction value, orientation degree, and impurities. The results obtained were characterized using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

2. Research Methods

In this study, oxides and carbonates were used with a high level of purity, namely: Bi_2O_3 (99.9%); PbO (99.9%); SrCO₃ (99.9%); CaCO₃ (99.95%); CuO (99.99%), HNO₃, equates, and HCl. The composition of the starting materials for making 3 grams of superconducting sample BPSCCO-2212 is presented in **Table 1**.

The tools used in this study were: digital sartorius balance, grinding tool (pastle and mortar), furnace, the crucible, spatula, sample mold (die), pressing tool, X-Ray Diffraction (XRD) type X 'Pert Powder Diffractometer, and Scanning Electron Microscopy (SEM) Type Vega Tescan.

The basic materials used in this study were weighed first according to the calculations in **Table 1.** After the material was weighed, then the material was dissolved with 68% nitric acid (HNO3), and distilled water was stirred slowly until the solution was clear blue. The material iwasplaced on a *hot plate* at 70 °C. Then, the solution was allowed to stand for 24 hours until the solution stirred. Drying was carried out gradually in a furnace at temperatures 300, 400, and 600 °C until the material was dehydrated.

After the material was dried in the furnace, grinding is carried out with mortar and pastel gradually for ± 10 hours until the material feels smooth. The sample was compacted with a pressing tool with a strength of 8 tons. After the sample is in the form of pellets, it is then calcined at a temperature of 800 °C for ± 10 hours. The calcined sample was not perfect due to porosity and surrounding gas capture, so it needed to be re-grinded for ± 10 hours. Then the sample was re-compacted and sintered with time variations of 10, 20, 30, and 40 hours at a temperature of 830 C to form the desired phase.

The results of the superconductor synthesis were then characterized using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). XRD characterization aims to determine the level of phase purity by calculating Fv, P, and I using the equation (1) to (3).

Starting Material	Fraction	Mass Count Each 3 gr sample (gr)	
D: 0	1.6	1.2353	
$B_{12}O_3$	1.6	0.1315	
PbO	0.4	0.8687	
$SrCO_3$	2.0	0.0007	
CaCO ₃	1.1	0.2948	
CuO	2.0	0.4686	
Total	1	3 0000	

Table 1. Material composition Bi 1.6 Pb 0.4 Sr 2 Ca 1.1 Cu 2 O

$$Fv = \frac{\sum I(2212)}{Itotal} \times 100\%$$
(1)

$$P = \frac{\sum I(001)}{\sum I(2212)} \times 100\%$$
 (2)

$$I = 100\% - Fv$$
 (3)

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where

F_{v}	= BPSCCO-2212 phase volume fraction
Р	= degree of orientation
Ι	= Impurity
I_{total}	= Total intensity
I ₍₂₂₁₂₎	= Phase intensity 2212
$I_{(001)}$	= BPSCCO-2212 phase intensity, with h = k = 0 and l an even number

XRD spectrum analysis was performed using the High Scoreplus program. SEM characterization aims to determine the microstructure of the BPSCCO-2212 superconductor.

3. Results and Discussions

3.1 Results of Characterization of X-Ray Diffraction (XRD)

To facilitate data presentation and analysis, each sample was coded based on the sintering time indicating the parameters of the synthesis process in the following format: BPSCCO-2212/10 hours indicates that the BPSCCO-2212 superconducting sample sintered for 10 hours.

The results of the XRD spectrum analysis of the BPSCCO-2212 sample are shown in **Figure 1**. Based on **Figure 1**. all the samples that have been synthesized succeeded in forming the BPSCCO-2212 phase, although they still did not form a pure BPSCCO-2212 phase, or many impurities appeared. In addition, all samples were oriented, indicating the presence of BPSCCO-2212 phase peaks with h = k = 0 and $\ell =$ even numbers. The results of the analysis of the High Scoreplus program and calculations using equations 1, 2, and 3 obtained the level of phase purity which includes volume fraction (Fv), degree of orientation (P), and impurity (I) for each sample.

Based on Figure 1, the resulting peaks consist of BPSCCO-2212 superconducting peaks and impurities. The BPSCCO-2212 peak is symbolized by A, while the impurity is symbolized by B and C. In general, all of the synthesized samples succeeded in forming the BPSCCO-2212 phase, although they still did not form a pure BPSCCO-2212 phase or many impurities appeared.

The BPSCCO-2212/10-hour sample formed 14 highest peaks with eight prominent peaks of BPSCCO-2212; four were impurities ($Ca_{5.54}Sr_{3,82}Bi_{0.04}$)Cu_{15.158}O_{28.321} and 2 peaks were impurities Bi_2O_4 . In the BPSCCO-2212/20 hour sample, 18 highest peaks were formed with nine prominent peaks of BPSCCO-2212, four peaks were Bi-2223 impurities, and 5 were compounds $Ca_{8.2}Sr_{5.8}Cu_{23.62}Bi_{0.38}O_{41}$. Then, the BPSCCO-2212/30-hour sample formed 17 highest peaks with ten prominent peaks of BPSCCO-2212, two peaks were Bi-2223 impurities, three were Ca compounds $Cu_2Sr_2Bi_2O_{8+x}$, and two peaks were impurities ($Bi_{1.8}Pb_{0.2}$)Sr₂CuO₆. In comparison, the BPSCCO-2212 / 40-hour sample formed 18 highest peaks with 14 prominent peaks of BPSCCO-2212 and four impurity peaks $Bi_2(Sr_2Ca_{0.4})CuO_6$.

The addition of sintering time to the sample can affect the phase formation in the BSCCO system (Nurmalita, 2011). Based on the results of XRD analysis, the purity of the BPSCCO-2212 phase formed in the form of volume fraction (Fv), orientation degree (P), and impurity (I), as shown in **Table 2** and **Table 3** shows that the sintering time is exceptionally influential on the formation of the superconducting phase of BPSCCO-2212. It can be seen in Table 2 that the value of the volume fraction is opposite to the value of the impurity. In BPSCCO-2212, with a sintering time of 40 hours, the highest volume fraction value was 86.72%, and the lowest impurity was 13.28%. Meanwhile, in BPSCCO-2212, with a sintering time of 30 hours, the lowest volume fraction value was 53.07%, and the highest impurity was 46.93%. In addition, BPSCCO-2212, with a sintering time of 10 hours, obtained a volume fraction value of 66.21%, and BPSCCO-2212, with a sintering time of 20 hours, had a volume fraction. Excess can form an impurity phase. This effect affects the formation of a phase with a sintering time of 30 hours BPSCCO-2212.

This research using the wet mixing method produces peaks that are clearer than the solids method carried out by Pratiwi (2017). The volume fraction results obtained in this study were 67.80% at a sintering time of 20 hours. Meanwhile, in this study, the volume fraction obtained at 20 hours of sintering was 59.66% and the highest volume fraction obtained at 40 hours of sintering was 86.72%. This shows that the synthesis of superconductors using the wet mixing method can increase the high homogeneity to get a higher phase purity.



Figure 1. X-Ray Diffraction (XRD) analysis results (a) BPSCCO-2212/10hours; (b) BPSCCO-2212/20hours; (c) BPSCCO-2212/30hours; (d) BPSCCO-2212/40hours. (Remarks: (A) BPSCCO-2212, (B) BSCCO-2223, (C) Impurities.

Table 2. Results of calculation of volume fraction and impurities

Sample Code	Phase Intensity 2212	Total intensity	Volume fraction (%)	Impurities (%)
BPSCCO -2212 / 10 hours	4959.4596	7490.5841	66.21	33.79
BPSCCO -2212 / 20 hours	3806.9762	6381.5696	59.66	40.34
BPSCCO -2212 /30 hours	24430,2609	32082,2882	53.07	46.93
BPSCCO-2212 / 40hours	19714,733	24934,558	86.72	13.28

Table 3. Orientation degree calculation result

Sample Code	$_{2} heta$	hkl (00 🦺	Intensity (00 🖡)	Degree of Orientation (%)
BPSCCO-2212/10hours	60.9618	00 <u>20</u>	427.5377	8,62
BPSCCO-2212/20 hours BPSCCO-2212/30 hours	23.3332	00 18	430,4325	13.59
, , , , , , , , , , , , , , , , , , , ,	29.2581	00 <u>10</u>	,	
BPSCCO-2212/40jam	23.1423 29.1511 36.8195	008 00 <u>10</u> 00 <u>10</u>	943,1525	11.67

3.2 Scanning Electron Microscopy (SEM) Characterization Results

Microstructure testing was carried out on all BPSCCO-2212 superconducting samples at various sintering times using Scanning Electron Microscopy (SEM). Each sample was recorded at a magnification of 2000×. The results of the SEM recording are shown in Figure 2.

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Figure 2. Results of Scanning Electron Microscopy (SEM) characterization (a) BPSCCO-2212/10 hours; (b) BPSCCO-2212/20 hours; (c) BPSCCO-2212/30 hours; (d) BPSCCO-2212/40hours.

Based on Figure 2, all samples did not show oriented layers. In addition, the samples showed poor crystal formation, and there were still lots of empty spaces between the plates (voids). The plates were seen to be oriented shown in Figure 12 (c), namely the BPSCCO-2212/30-hour sample. This follows the resulting orientation degree value of 13.59%. Meanwhile, the results that could be better oriented are shown in Figure 12 (b). It can be seen that many of the characterization results have yet to form unidirectional plates with a degree of orientation value of 7.67%. The degree of orientation resulting from variations in the sintering time is irregular. It follows the SEM characterization results, which show that the plate image is also not improving.

4. Conclusion

Based on the results of XRD characterization, the highest volume fraction was obtained at a sintering time of 40 hours BPSCCO/40 hours at 86.72%. Meanwhile, at a sintering time of 30 hours BPSCCO/30 hours, the lowest volume fraction value was 53.07%.

In addition to the BPSCCO-2212 phase, other phases were obtained, namely BPSCCO-2223 and other impurities, at sintering times of 10, 20, 30, and 40 hours.

The SEM test results show that the variation of sintering time affects the surface morphology of the resulting more homogeneous superconductor and the plates tend to be oriented (oriented) based on the results of the degree of orientation produced with the highest value of BPSCCO-2212/30 of 13.59% and the lowest degree of orientation of BPSCCO-2212/ 20 hours by 7.67%.

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